

Critical Fluctuation Universality in Chemically Oscillatory Systems: A Soluble Master Equation

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Multiple time scale arguments are used to show that near a Hopf bifurcation to a chemical oscillation the dynamics of the system reduces to that of a classic soluble limit cycle system. A birth and death master equation is then introduced and the spectrum of the resulting transition operator is shown to be complex. Exact solutions of the master equation are obtained both for the steady and (for a rather general class of systems) "excited" states. Thus a simple basis of universality of critical properties in chemical oscillations is provided.

KEY WORDS: Chemical oscillations; critical fluctuations; master equation; critical universality; limit cycle; chemical instability; dissipative structure; scaling theory.

1. INTRODUCTION

Limit cycle oscillations have been found in chemically reacting systems⁽¹⁾ as well as in electrical circuits,⁽²⁾ lasers,⁽³⁾ and insect flight.⁽⁴⁾ As these systems are driven sufficiently far from equilibrium, oscillation may either set in as a normal (i.e., not inverted) Hopf bifurcation^(5,6)—i.e., as a smooth (second-order) transition where the amplitude of oscillation increases continuously from zero as one passes beyond the bifurcation point. Alternatively, oscillations may set in as a first-order transition,⁽⁷⁾ where a system passes from a steady state to one with a homoclinic orbit to a large-amplitude oscillation as a parameter passes through the transition point. Alternatively a pair of cycles, one stable and one unstable, may emerge from a neutrally stable cycle that arises at a bifurcation point at finite amplitude from a stable steady state. The analogy of transitions between nonequilibrium states and that of equilibrium phase transitions has been discussed elsewhere.⁽⁸⁾

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In this paper we consider the case of a normal Hopf bifurcation to a limit cycle. In this case the system has a nonequilibrium critical point at the onset of oscillation. It is known that such nonequilibrium critical points have a close analogy to equilibrium phase transition critical behavior.⁽⁸⁾ Of particular interest is the presence of critical fluctuations—i.e., long-lived fluctuations about average values of the state variables such as concentrations, temperature, or pressure.

In Section 2 we use scaling arguments^(9–13) to show that sufficiently close to the critical point the equations of reaction and diffusion for an arbitrary reacting system reduce to a time-dependent Ginzburg–Landau (TDGL) equation for a complex order parameter, in agreement with earlier reductive perturbation methods which were applied to a special case.⁽⁹⁾ We then generalize an earlier result,⁽¹³⁾ finding that the equation for the complex order parameter reduces to a classic soluble model nonlinear oscillator equation⁽¹⁴⁾ studied earlier in the context of the theory of nonlinear chemical waves.^(15–17)

A master equation is introduced in Section 3 to describe fluctuations in the classic oscillator and it is argued that this equation should describe critical behavior in general systems at a normal Hopf bifurcation. It is shown that the spectrum of the transition operator is complex, and the existence of damped excitations which rotate around the phase plane trajectory is demonstrated. The universal oscillator master equation is shown in Section 4 to yield exact solutions for the steady state and, in a somewhat restricted case, for excited states.

Finally, in Section 5 the expected universality of critical exponents for oscillatory systems is used to argue that the present model of fluctuations contains all the interesting critical behavior for a normal Hopf bifurcation but that other oscillator-fluctuation-like systems—i.e., homoclinic, chaotic, and unstable cycles—remain as important outstanding problems in the theory of fluctuations. Other treatments of fluctuations in limit cycle systems are to be found in Refs. 8, 23, and 29–32.

2. SCALING AND THE UNIVERSAL LIMIT CYCLE/WAVE EQUATION

The excitations of a system near a critical point that are known to lead to critical behavior are those whose lifetime diverges as we approach the critical point. Thus in order to describe critical behavior it is important to deduce an equation of motion (EOM) for these excitations. The scaling method and the closely related reductive methods^(9–13) are techniques for deriving such EOMs.

We start with the reaction diffusion equation for a system of N species, $i = 1, 2, \dots, N$, with concentrations $c(\mathbf{r}, t) = \{c_1, c_2, \dots, c_N\}$; we have

$$\partial c / \partial t = D \nabla^2 c + \Omega c + \mathcal{N}(c) \tag{2.1}$$

where we assume that c is measured with respect to a homogeneous steady state, D is a matrix of diffusion coefficients, Ω is a matrix of the linearized reaction rates, and \mathcal{N} is a column vector of nonlinear rate contributions of second or higher order in c . It is useful to introduce a set of mode coordinates $M_\alpha(\mathbf{r}, t)$ measuring the amplitudes of the eigenvectors of Ω ,

$$\Omega|\alpha\rangle = \gamma_\alpha|\alpha\rangle \tag{2.2}$$

(and similarly for $\langle\alpha|$) in terms of the development

$$c(\mathbf{r}, t) = \sum_\alpha M_\alpha(\mathbf{r}, t)|\alpha\rangle \tag{2.3}$$

Putting this development into (2.1), we obtain

$$\partial M_\alpha / \partial t = \sum_\beta \mathcal{D}_{\alpha\beta} \nabla^2 M_\beta + \gamma_\alpha M_\alpha + \sum_{\beta, \beta'} N_{\alpha\beta\beta'} M_\beta M_{\beta'} \tag{2.4}$$

$$\mathcal{D}_{\alpha\beta} = \langle\alpha|D|\beta\rangle \tag{2.5}$$

$$N_\alpha^{\beta\beta'} = \sum_{i,j,k=1}^N i \langle\alpha|N_{i,j,k}|\beta\rangle_j |\beta'\rangle_k \tag{2.6}$$

where for simplicity we assume that $N(c)$ is quadratic, $N_i(c) = \sum_{j,k=1}^N N_{i,j,k} c_j c_k$.

For the existence of a Hopf bifurcation there must be a pair of complex roots $\gamma_{1,2} \equiv \gamma_\pm$ such that

$$\gamma_\pm = \pm i\omega + \gamma \tag{2.7}$$

where γ passes through zero as a constraint parameter λ passes through a critical value λ_c and the frequency $\omega \neq 0$. The scaling approach proceeds by introducing scaled variables according to

$$\mathbf{r}' = s^{-1}\mathbf{r}, \quad t' = s^{-z}t, \quad \gamma' = s^u\gamma \tag{2.8}$$

and seeking solutions in the form

$$\begin{aligned} M_+(\mathbf{r}, t, \gamma) &= s^{-x} W(\mathbf{r}', t', \gamma') e^{i\omega' t'} \\ M_- &= M_+^* \\ M_\alpha(r, t, y) &= s^{-x_\alpha} M_\alpha(r', t', \gamma'), \quad \alpha \neq \pm \end{aligned} \tag{2.9}$$

The conjecture one makes in taking the scaling ansatz (2.9) is that there exist solutions which can be described as an oscillator with an amplitude and phase that vary slowly in space and time through the function W that will be found to play the role of a complex order parameter for the present system. The scaling exponents z, u, x , and x_α are determined by ensuring that the

class of solutions determined by a given choice yield equations of motion yield a class of solutions which are nontrivial as the space scaling factor s diverges and hence, since $u > 0$, $\gamma = s^{-u}\gamma' \rightarrow 0$ as $s \rightarrow \infty$ and the system is arbitrarily close to the critical point.

Upon substituting the scaling ansatz into the equation of motion (2.4) for the mode coordinates, we find that the long-lived critical excitations we seek are solutions of the equations (dropping the primes)

$$\partial W/\partial t = \mathcal{D} \nabla^2 W + \gamma W + b|W|^2 W \tag{2.10}$$

where we have used the choice

$$z = u = x_\alpha = 2x = 2 \tag{2.11}$$

for the scaling exponents; also, one must use the fact that terms with factors $e^{i\omega' t}$, $\omega' = s^2\omega$, will, as $s \rightarrow \infty$, average out when in an equation of motion of a slowly evolving variable.

The constant coefficients in the TDGL equation (2.10) are given by

$$\mathcal{D} = \langle +|D|+ \rangle \tag{2.12}$$

$$b = -2 \sum_{\alpha \neq \pm} N_+^{+\alpha} N_\alpha^{+-} / \gamma_\alpha \tag{2.13}$$

Note that in general the order parameter “diffusion coefficient” may be complex and furthermore its real part may be negative, indicating a symmetry-breaking instability, as was found for the pattern formation instability in the competitive particle growth theory of Liesegang banding.⁽²⁷⁾ These results are in agreement with those obtained by reductive perturbation theory^(4,27) (although in Ref. 13 it appears that \mathcal{D} is assumed real).

The Soluble Universal Cycle

It has been pointed out⁽¹³⁾ that the TDGL equation of the form (2.10) is closely related to a classic limit cycle system⁽¹⁴⁾ studied by several authors as a soluble model for chemical waves.⁽¹⁵⁻¹⁷⁾ In order to show the relationship to and to introduce the classic limit cycle system we define the modulus and phase of W ,

$$W = R e^{i\theta} \tag{2.14}$$

Introducing real quantities

$$\mathcal{D} = \mathcal{D}_1 + i\mathcal{D}_2, \quad b = b_1 + ib_2 \tag{2.15}$$

and substituting (2.14) into the TDGL equation for W , we find

$$\partial R/\partial t = \mathcal{D}_1[\nabla^2 R - R|\nabla\theta|^2] + \mathcal{D}_2[2\nabla R \cdot \nabla\theta + R\nabla^2\theta] + RB(R) \tag{2.16}$$

$$R \partial \theta / \partial t = \mathcal{D}_1 [2 \nabla R \cdot \nabla \theta + R \nabla^2 \theta] + \mathcal{D}_2 [\nabla^2 R - R |\nabla \theta|^2] + A(R) \quad (2.17)$$

$$A(R) = b_2 R^3, \quad B(R) = \gamma + b_1 R^2 \quad (2.18)$$

(If we neglect the complex part of \mathcal{D} , $\mathcal{D}_2 = 0$, we obtain the results of Ref. 13, although \mathcal{D}_2 may be nonzero for the more general case.)

Equations of this form, with $\mathcal{D}_2 = 0$, have been studied as a polar transformation of reaction-diffusion equations for the variables $X = R \cos \theta$, $Y = R \sin \theta$.⁽¹⁵⁻¹⁷⁾ In these studies it has been found that plane wave solutions can be found in the form of constant-amplitude solutions $R = R_0$, $B(R_0) - k^2 \mathcal{D}_1 = 0$ with frequency $A(R_0)$ and phase $\theta = \mathbf{k} \cdot \mathbf{r} + A(R_0)t$. Similar solutions exist for (2.17) except that for $\mathcal{D}_2 \neq 0$ there is a diffusion correction to the frequency, which is $A(R_0) - k^2 \mathcal{D}_2$, \mathbf{k} being the wave vector for the wave. It was emphasized in Ref. 17 that for the more general choices of $B(R)$ one could find soluble examples exhibiting multiple wave solutions, excitability, and even waves of variable amplitude. Furthermore, in Ref. 13 the existence of spiral waves in this system was proved and in Ref. 28 the model was analyzed via a Padé approximant scheme to generate explicit periodic and aperiodic center wave solutions. Static structures were also studied in Ref. 4, and, furthermore, exactly soluble, multiply periodic reaction-diffusion patterns were found on a closely related three-variable "polarator" model.⁽²⁵⁾

Thus it is quite interesting that near a critical point a general oscillatory system reduces to a very tractable but nontrivial nonlinear problem which demonstrates many nonlinear wave, pattern, and chaotic phenomena. The success in finding these analytic solutions of the deterministic model suggests the possibility that this system may lead to a soluble master equation characterizing fluctuations for a general oscillatory system sufficiently close to the critical point. This is the subject of the next two sections.

3. FLUCTUATIONS IN THE UNIVERSAL MODEL

The universal model has been shown to describe the long-lived fluctuations near the critical point. Let us now set forth a statistical equation based on this model. Perhaps the most well-accepted theory of fluctuations in nonequilibrium reacting systems is the cell master equation based on the birth and death model⁽²⁰⁾ extended to include diffusion.⁽²¹⁾ Rather than attempt a derivation of such an equation from this starting point, we make the assumption here that an adequate model of fluctuations can be constructed in terms of the polar coordinates R and θ discussed above. Since these coordinates were found advantageous for finding exact solutions in the case of chemical waves and oscillations,⁽¹⁵⁻¹⁷⁾ one might expect that a statistical theory based on them would be soluble.

3.1. A Master Equation

Fluctuations in nonequilibrium reacting systems have, for the most part, been described by birth and death master equations in the particle number variables. We would like to derive a statistical equation in the R, θ variables from a particle number master equation since one might expect that, as for the ordinary differential (macroscopic) equations, the problem might be separable. It is known from the theory of equilibrium critical phenomena that properties such as critical exponents are insensitive to the details of the Hamiltonian and hence of the statistical model (since the probability distribution depends on the Hamiltonian). Furthermore, the particle number birth and death master equation for chemical reactions has not been justified from statistical mechanics but is a postulated statistical model. Likewise here we postulate a birth and death type formalism in the R, θ variables, recognizing that it may not necessarily be identical to the statistical model derived by appropriate transformation from the (yet unproven) particle number formalism. As in the latter, the construct shall ensure the existence of the correct macroscopic equations in the small-fluctuation limit and it is furthermore reasonable to expect that a certain universality should exist for, say, critical exponents which will justify the use of the model.

To construct our statistical model we invoke the spirit of the birth and death master equation and further require that the most probable trajectory away from any critical behavior should obey the macroscopic equations of motion. We start by introducing a polar grid consisting of L rays from the origin separated by an angle $\Delta\theta$ such that

$$L \Delta\theta = 2\pi \quad (3.1)$$

Furthermore, the R coordinate is broken up into steps separated by jumps ΔR . Thus the allowed states of the system are the vertices of the polar grid shown in Fig. 1.

The statistical model consists of a master equation for the probability $\mathcal{P}(n, j, t)$ for the system to be at $\theta = n\Delta\theta$, $R = j\Delta R$, where $n = 0, 1, \dots, L$ and $j = 1, 2, \dots$. The point $j = 0$ at the origin has been excluded since in any real system the center of a macroscopic limit cycle corresponds to a fraction of a particle anyway and hence is not accessible. Because of the polar geometry of the grid we note the periodic boundary condition

$$\mathcal{P}(n + L, j, t) = \mathcal{P}(n, j, t) \quad (3.2)$$

a constraint which will play the same role in determining the eigenvalues of the transition operator that rotational symmetry does for, say, the two-dimensional central force problem in quantum mechanics.

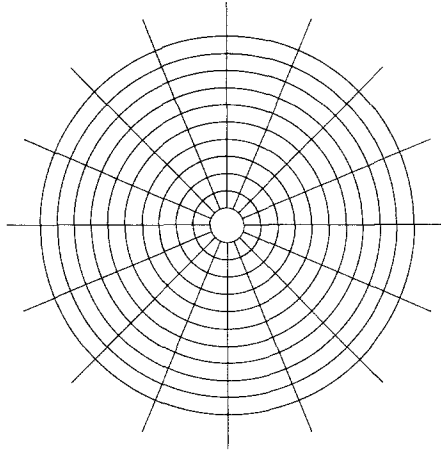


Fig. 1. Polar grid for “birth and death” master equation (3.2).

Using a birth and death type formalism with transition rates obtained from the macroscopic equations of motion (2.16) and (2.17) we obtain the following master equation:

$$\begin{aligned} \partial \mathcal{P}(n, j, t) / \partial t = & \tilde{A}_j [\mathcal{P}(n-1, j, t) - \mathcal{P}(n, j, t)] \\ & + \lambda_1 [(j-1) \mathcal{P}(n, j-1, t) - j \mathcal{P}(n, j, t)] \\ & + \lambda_2 [(j+1) \mathcal{P}(n, j+1, t) - j \mathcal{P}(n, j, t)] \\ & + \tilde{B}_{j+1} \mathcal{P}(n, j+1, t) \\ & - \tilde{B}_j \mathcal{P}(n, j, t), \quad j \geq 2 \end{aligned} \tag{3.3}$$

$$\begin{aligned} \partial \mathcal{P}(n, 1, t) / \partial t = & A_1 [\mathcal{P}(n-1, 1, t) - \mathcal{P}(n, 1, t)] \\ & - \lambda_1 \mathcal{P}(n, 1, t) + 2\lambda_2 \mathcal{P}(n, 2, t) \\ & + \tilde{B}_2 \mathcal{P}(n, 2, t) \end{aligned} \tag{3.4}$$

$$\lambda = \lambda_1 - \lambda_2, \quad \lambda_1, \lambda_2 > 0 \tag{3.5}$$

$$\tilde{A}_j \equiv A(j \Delta R) / \Delta \theta \tag{3.6}$$

$$\tilde{B}_j = b_1 \Delta R^2 j^2 \tag{3.7}$$

One may show that if fluctuations are neglected this stochastic equation leads to (the space-independent part of) (2.16) and (2.17) for the evolution of the most probable—deterministic—trajectory. Note that to construct a more general class of soluble fluctuating oscillator systems we may take B to be arbitrary and generate the richness of phenomena found in Refs. 4 and 17.

3.2. Eigenfunctions of the Transition Operator

One of the features of (3.3) that allows for exact solution is that the eigenfunctions of the transition operator may be written as a product of n - and j -dependent distributions, i.e., there are solutions of (3.3) in the form

$$\mathcal{P}(n, j, t) = \Theta(n)\mathcal{R}(j)e^{zt} \quad (3.8)$$

To carry out the usual separation of variables scheme we write (3.3) in the form

$$\partial\mathcal{P}/\partial t = \mathcal{A}\mathcal{P} + \mathcal{V}\mathcal{P} \quad (3.9)$$

where $\mathcal{A}(j)$ only operates on the θ index n and \mathcal{V} only operates on the R index j {i.e., $\mathcal{A}\mathcal{P}(n, j, t) = \tilde{A}_j[\mathcal{P}(n-1, j, t) - \mathcal{P}(n, j, t)]$ } and \mathcal{V} is defined by comparing (3.3) and (3.9). With this we find that for eigenvalues σ to be determined shortly, $\Theta(n)$ and $\mathcal{R}(j)$ must satisfy the equations

$$\Theta(n-1) - \Theta(n) = \sigma\Theta(n) \quad (3.10)$$

$$[\tilde{A}_j\sigma + \mathcal{V} - z]\mathcal{R}(j) = 0 \quad (3.11)$$

Taking the complex conjugate of (3.10), it is seen that for each solution (Θ, σ) there is, for complex σ , a second solution (Θ^*, σ^*) . Hence the angular eigenvalues are distributed symmetrically about the $\text{Im } \sigma = 0$ axis in the complex σ plane. Similarly, for every solution (\mathcal{R}, σ, z) there is a solution $(\mathcal{R}^*, \sigma^*, z^*)$ and hence the eigenvalues and eigenfunctions of the transition operator are either real or occur in complex conjugate pairs (since the transition operator is real). Let us analyze the two equations separately.

3.2.1. The Angular Eigenvalues. The difference equation (3.10) is trivial and yields the solution

$$\Theta(n) = \Theta(0)/(1 + \sigma)^n \quad (3.12)$$

As in quantum mechanics or electromagnetic theory the rotational symmetry fixes the eigenvalues; the periodicity condition (3.2) yields $(1 + \sigma)^L = 1$, and introducing L roots of unity,

$$u_q = e^{2\pi i q/L}, \quad q = 0, 1, \dots, L-1 \quad (3.13)$$

we obtain

$$\sigma_q = u_q - 1 \quad (3.14)$$

Substituting this value for σ_q into (3.11), we obtain an equation for the eigenfunctions $\mathcal{R}_q(j)$, which are seen to be the null vectors of a complex transition operator.

3.2.2. The Case $\tilde{A} = \text{const.}$ The most general case where A depends on j will not be considered further in this section. In contrast to

the general case, the simplest case of constant A lends itself to easy analysis. Furthermore, the variation of the frequency as a chemical oscillation bifurcates is a nonessential feature of the problem and should not dramatically affect the results except in rather exceptionally strong dependences. In any case we can typically vary experimental parameters such that a bifurcation occurs but the frequency is essentially constant.

From (3.11), $\mathcal{R}_q(j)$ are seen to be the eigenfunctions of \mathcal{V} with eigenvalue v ,

$$v = z - \tilde{A}\sigma_q, \quad \mathcal{V}\mathcal{R}(j) = v\mathcal{R}(j) \quad (3.15)$$

From its character we can take \mathcal{V} to have a real spectrum bounded from above by and including zero.

It is instructive to consider the case $v = 0$, the steady state of the radial distribution $\mathcal{R}^0(j)$ (and in fact for the full system—see next section). Thus for these eigenfunctions

$$z_q = \tilde{A}\sigma_q, \quad \mathcal{R}(j) = \mathcal{R}^0(j) \quad (3.16)$$

In particular in the “thermodynamic limit” $\Delta\theta \rightarrow 0$, $L \rightarrow \infty$ we have for q finite

$$z_q = \tilde{A}\sigma_q \sim Aqi - \pi Aq^2/L \quad (3.17)$$

Thus the lowest-lying “excitation” from the $z = v = 0$ (steady) state, $q = 1$, is seen to oscillate with the frequency of the deterministic oscillator and to damp on a very long time scale, $L/\pi A$.

Note that the limits $L \rightarrow \infty$ and $t \rightarrow \infty$ do not commute. For a finite system, $L < \infty$, the probability always damps out to the steady distribution \mathcal{R}^0 . However, taking $L \rightarrow \infty$ first, we see that the probability will oscillate indefinitely.

To see the character of the $q = 1$ mode we note that combining the $q = 1$ mode and its complex conjugate $q = -1$, we obtain the real-valued distribution ($L \gg 1$)

$$\mathcal{R}^0(j) \cos(At - 2\pi n/L) e^{-\pi At/L} \quad (3.18)$$

which is seen to rotate at the cycle frequency A and to have one maximum moving at the position $n = Lat/2\pi$. As we shall show below, beyond the bifurcation point, $\lambda > 0$, $\mathcal{R}^0(j)$ has a sharp maximum at j_{\max} around the cycle amplitude predicted by the macroscopic equations, i.e., around $B(j_{\max} \Delta R) = \lambda$. This behavior explains, on a statistical basis, how a limit cycle can carry out its deterministic motion for long times before an ensemble of systems reaches the state $\mathcal{R}^0(j)$ with the phase of oscillation distributed, uniformly in the present simple model, around the deterministic cycle.

Finally, for the simple case $A = \text{const}$ we see that the eigenvalue spectrum of the transition operator is as shown in Fig. 2. Note that for a large system ($L \gg 1$) the spectrum (for a given v) is continuous and in the left half-plane.

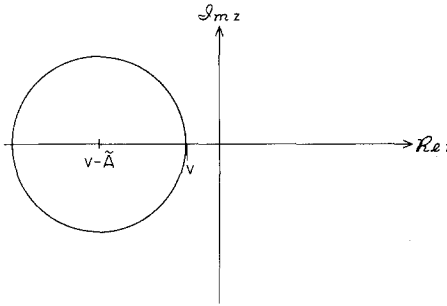


Fig. 2. Eigenvalues of the birth and death master equation for the limit cycle system.

3.2.3. R -Dependent Frequency. For the case $A = A(R)$ the analysis is much more difficult. It is tempting to conjecture that the spectrum again lies on arcs in the left half-plane with “low-lying states” having an eigenvalue with small negative real part and imaginary part of the order of magnitude of the macroscopic cycle frequency. Furthermore, one may show for $q \neq 0$ (by dividing R_j into real and imaginary parts) that there are no nontrivial solutions (3.11) for real z . Also, we may, as mentioned above, often set experimental conditions so that the frequency function A only depends weakly on R . This suggests that we can write $A(R) = \tilde{A} + \Delta A(R)$ and do a perturbation theory in $\Delta A(R)$. Clearly in this limit the above conjectures are justified. However, if A depends very strongly on R a more careful analysis is needed.

4. THE CRATER DISTRIBUTION

One might expect that the steady-state probability distribution for a limit cycle would have the appearance of a ridge or crater with maximum describing the orbit of the deterministic cycle. In this section we explicitly show this and other properties of the universal cycle master equation by obtaining an exact solution for the steady state.

The Steady-State Distribution

As shown in the previous section, the angle-dependent states are time dependent. The steady-state distribution for this system $\mathcal{P}^0(j)$ is independent of the angular index and obeys the equation

$$\Phi_{j+1} - \Phi_j = 0, \quad j \geq 2 \quad (4.1)$$

$$\Phi_j \equiv -\lambda_1(j-1)\mathcal{P}^0(j-1) + [\lambda_2 j + \tilde{B}_j]\mathcal{P}^0(j) \quad (4.2)$$

We shall solve this equation for arbitrary $B(R)$. For the universal oscillator we have specifically

$$\tilde{B}_j^{\text{univ}} = b_1 \Delta R^2 j^3 \tag{4.3}$$

Equation (4.1) implies that Φ_j is independent of j , i.e., for some constant c we have

$$\Phi_j = c \tag{4.4}$$

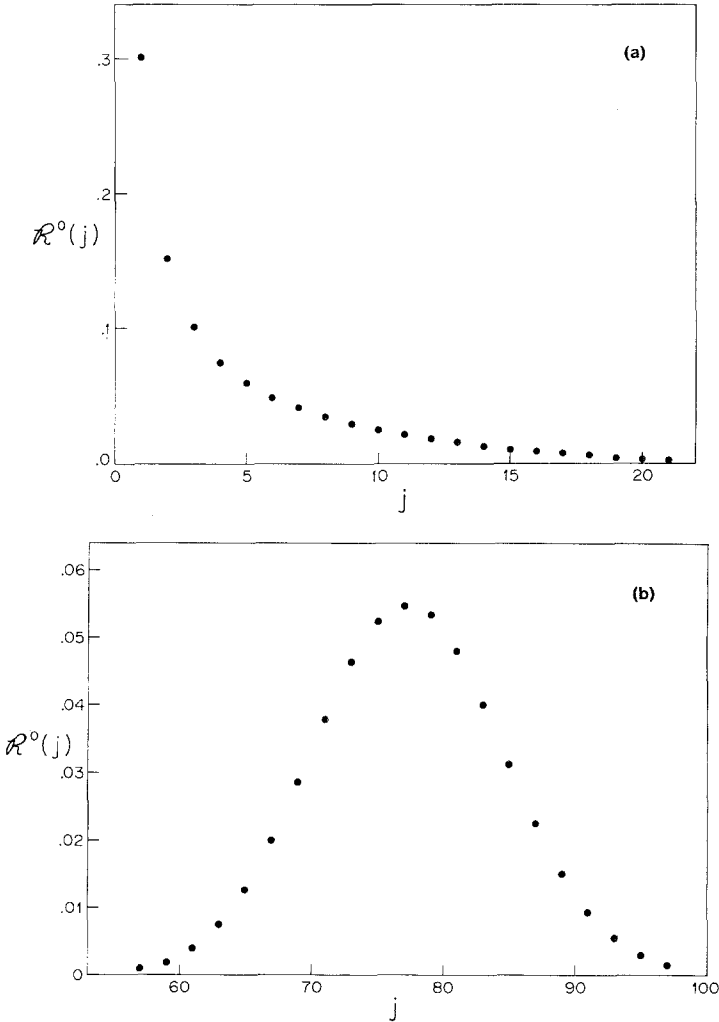


Fig. 3. Steady-state probability distributions $\mathcal{R}^0(j)$ for universal model (4.3), (4.6). In terms of reduced parameters $\mu_\alpha = \lambda_\alpha/b_1 \Delta R^2$, $\alpha = 1, 2$, the cases of (a) the critical state $\mu_1 = \mu_2$ and (b) a stable limit cycle (at $\mu_1 = 8192$) are shown for the choice $\mu_2 = 2048$. For a stable steady state at $\mu_1 = 512$ the distribution (not shown) is very narrow, being centered around $j = 1$ with a width of 0.448.

We may show that $c = 0$ by first noting that from (3.1) the equation for $\mathcal{R}^0(1)$ reads

$$0 = -\lambda_1 \mathcal{R}^0(1) + 2\lambda_2 \mathcal{R}^0(2) + \tilde{B}_2 \mathcal{R}^0(2) \quad (4.5)$$

and evaluating (4.3) and (4.4) for $j = 2$ we find, on comparison with (4.5), that $c = 0$. Thus (4.4) becomes $\Phi_j = 0$ and using (4.3), we find upon recurring

$$\frac{\mathcal{R}^0(j)}{\mathcal{R}^0(1)} = \prod_{i=2}^j \frac{\lambda_1(i-1)}{\lambda_2 i + \tilde{B}_i} \quad (4.6)$$

For the universal model one may show for $\lambda_1 \gg \lambda_2 \gg 1$ that (using Stirling's approximation) there is a maximum in $\mathcal{R}^0(j)$ at $j_{\max} = \lambda/\Delta R^2$. Hence in the thermodynamic limit the cycle bifurcates with the classical value of $1/2$ for the bifurcation exponent, i.e., the power of the bifurcation parameter $\lambda = \lambda_1 - \lambda_2$ with which the amplitude of the cycle arises.

In Fig. 3 we show $\mathcal{R}^0(j)$ for parameters indicated in the legend. Below the critical point, $\lambda_1 < \lambda_2$, the distribution is sharply peaked about the origin. Far beyond the critical point the distribution has a maximum corresponding to the location of the macroscopic cycle. From the R, θ geometry it is seen that the steady-state distribution corresponds to a crater-like configuration. At the critical point the distribution is broad and centered about the origin.

5. REMARKS

It is interesting to conjecture that our statistical model of fluctuations in limit cycle systems developed in Sections 2 and 3 contains all the interesting behavior for these systems at least in the vicinity of the critical point. To argue in this direction we have to address several key questions. First the scaling arguments used to derive the TDGL equation were based on a phenomenological reaction-diffusion equation. This scaling approach is known^(11,12) to be strictly valid only in the mean field approximation. On the other hand, GL-type models have been used in the equilibrium theory of critical phenomena as Hamiltonians to generate probability functionals for determining static critical phenomena and in TDGL equations to study critical dynamic phenomena. One could argue that the well-known universality that exists for critical phenomena^(18,19) suggests that the details of the system do not determine the critical exponents. Thus it seems reasonable that one could argue that mean field type scaling can be used to generate an equation of motion for the critical point. Noise added to that TDGL equation will cause the scaling of fluctuations to change close to the critical point.

A second point to be addressed is the fact that the master equation presented in Section 3 is based on the R, θ variables and not derived from a

birth and death master equation for chemical species particle numbers.⁽²⁰⁾ It would be interesting to attempt such a derivation, although this is beyond the scope of the present study.

Our master equation has not been constructed to consider spatial variations. In future developments we shall consider the extension of our master equation in direct analogy to the cell master equations considered by other authors to generalize the master equation to include diffusion⁽²¹⁾ and furthermore to study questions of nucleation and fluctuations around a stable cycle via the nonlinear mean field master equation.⁽²²⁾ The properties of phase correlation have already been studied using a perturbed oscillator theory and a phenomenological Langevin equation.⁽²³⁾ It was found, for example, that a phase correlation length exists over which an oscillatory system could maintain phase coherence.

Perhaps the most interesting (and probably the most difficult) theoretical question in the subject is whether one can derive simple statistical criteria to distinguish among the following phenomena:

1. Critical fluctuations near a Hopf bifurcation to a limit cycle.
2. Fluctuations about a stable cycle.
3. Giant fluctuations in homoclinic systems.⁽⁷⁾
4. Spatiotemporal chaotic (strange attractor) behavior.^{(24,25),2}

It would be interesting, and useful in analyzing system kinetics, to see if, for example, the space-time composition autocorrelation functions for these systems were qualitatively different. Such quantities could possibly be determined from light scattering experiments⁽²⁶⁾ or more directly by using more macroscopic multichannel autocorrelation techniques.

A simple three-variable "polarator" model yielding exactly soluble, multiply periodic spatiotemporal reaction-diffusion solutions has been studied.⁽²⁵⁾ The model is essentially a three-dimensional extension of the R , θ model studied here and can be used to construct a master equation like that in Section 3 to study fluctuations in multiply periodic systems. It appears that this system should even be interesting in the context of strange attractors since it has been shown that an infinitesimal change in the equations of a system leading to multiply periodic behavior yields a strange attractor. Thus it is hoped that the present calculation plus its extension to the polarator should be useful in the study of fluctuations in oscillatory and chaotic systems.

² There is some work on statistical properties of Lorenz equations.

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